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ARPA Order No. 2721

TECHNICAL REPORT NO. 4

VALENCE PHOTOISOMERIZATION OF 1-ETHOXYCARBONYL-1H-AZEPINE:
EXCITED STATE ENERGETICS AND MULTIPLICITY

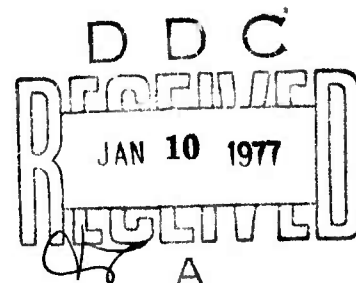
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Prepared for publication
in the
Journal of Photochemistry

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December 1, 1976



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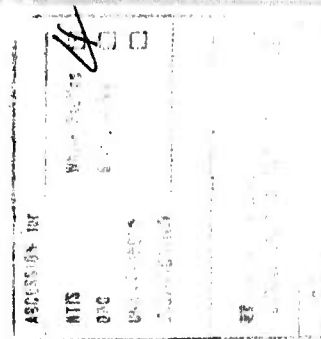
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 4, 19 Jul 74-31 May 75	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Valence Photoisomerization of 1-Ethoxycarbonyl-1H-azepine: Excited State Energetics and Multiplicity.	5. TYPE OF REPORT & PERIOD COVERED Technical, 7/1/74-5/31/75	
7. AUTHOR(s) Guilford Jones, II and Laura J. Turbini	6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, Boston University Boston, Massachusetts 02215	8. CONTRACT OR GRANT NUMBER(s) N00014-67-A0280-0003, ✓ ARPA Order - 2721	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 DODAAD Code N00014	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS ARPA Order No. 2721/1-4-74 Program Code No. 4F10	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 11 Dec 76 126p.	12. REPORT DATE December 1, 1976	
	13. NUMBER OF PAGES 4	
	15. SECURITY CLASS. (of this report) unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Reproduction in whole or in part is permitted for any purpose of the United States Government. Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Prepared for publication in the Journal of Photochemistry		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Valence photoisomerization, excited state configuration and multiplicity, photochemistry or heterocycles.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Photolysis of 1-ethoxycarbonyl-1H-azepine in solution at 325-385 nm gives a valence isomer with a quantum efficiency of 0.013. Valence photoisomerization cannot be driven with triplet photosensitizers nor can it be quenched by a triplet quenchers. The isomerization can be carried out using laser excitation at 458 nm. The azepine does not luminescence, but excited state energies can be estimated from absorption and sensitization data ($S_1 = 60$ kcal/mol, $T_1 = 55$ kcal/mol).		

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VALENCE PHOTOISOMERIZATION OF 1-ETHOXYCARBONYL-1H-AZEPINE.

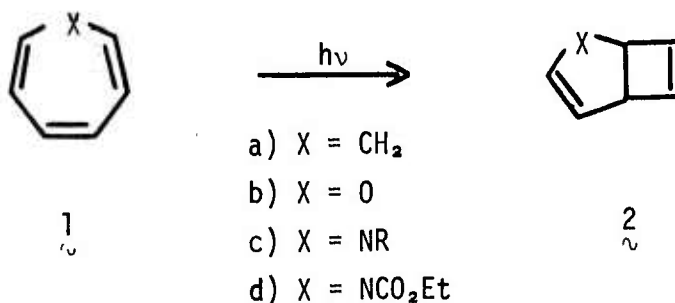
EXCITED STATE ENERGETICS AND MULTIPLICITY.

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The general importance of photochemical valence isomerization $1 \rightarrow 2$ for systems related to 1,3,5-cycloheptatriene is well recognized.¹ Quantitative studies directed to the identification of excited states responsible for isomerization and the general location of states for the cyclic trienes are rare. We supply here such detail concerning the previously reported^{1d} isomerization $1d \rightarrow 2d$. The absorption, photosensitization and quenching data fortuitously combine to provide quantitative information which is normally unavailable in the absence of triene luminescence.



Irradiation of $1d$ in the region of n,II* absorption² gave $2d$ in high yield. Quantum yields for isomerization in solution with and without additives are

Table. Quantum Yields for Photoisomerization $\underset{\sim}{1d} \rightarrow \underset{\sim}{2d}$.

[3]	Solvent	Additive (M)	ϕ^a
0.08	cyclohexane	----	0.010
0.09	diglyme	----	0.013
0.10	benzene	----	0.013
0.03	n-propyl bromide	----	0.013
0.08	benzene	cyclooctatetraene (0.11)	0.014
0.10	benzene	diene ^b (0.02-0.08)	0.012
0.10	benzene	fluorenone (0.9) (53) ^c	<0.003 ^d
0.09	benzene	benzophenone (1.0) (69) ^c	<0.003 ^d
0.007	benzene	valerophenone (0.4) (72) ^c	<0.003 ^d

^aRayonet reactor (325 - 385 nm), $30 \pm 1^\circ\text{C}$, valerophenone actinometer, estimated error $\pm 15\%$. ^b2,4-dimethyl-2,5-hexadiene ($E_T < 58 \text{ kcal/mol}$).

^cSensitizer E_T , kcal/mol. ^dUpper limit corrected for azepine absorption.

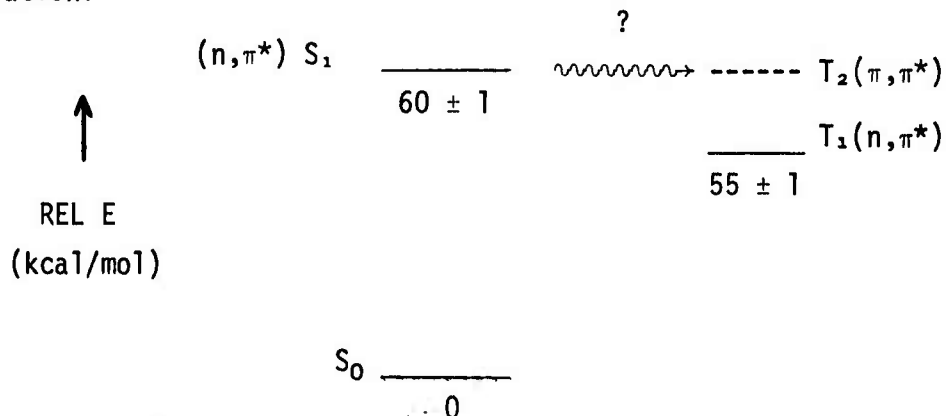
shown in the Table. The lack of quenching by diene and cyclooctatetraene (for which a very low triplet energy has been calculated³), along with the lack of sensitization in experiments where sensitizers absorbed >75% of the light, implicate a singlet excited state for valence isomerization of $\underset{\sim}{1d}$.

That a triplet state of $\underset{\sim}{1d}$ is available was inferred from its quenching behavior. Conventional Stern-Volmer analysis of the quenching of valerophenone photoelimination⁴ and biacetyl phosphorescence in benzene as a function of $[\underset{\sim}{1d}]$ gave $k_q \tau = 56 \pm 8$ and $2.5 \pm 0.3 \times 10^5 \text{ M}^{-1}$, respectively. Using triplet lifetimes of valerophenone ($8.0 \times 10^{-9} \text{ sec}$)⁴ and biacetyl ($4.6 \times 10^{-4} \text{ sec}$)⁵, quenching constants are calculated ($k_q = 7.0 \times 10^9$ and $5.3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$, respectively).

Photolysis of $\underset{\sim}{1d}$ in benzene near its onset of absorption using an argon ion laser (457.9 nm) gave $\underset{\sim}{2d}$ with a quantum yield of 0.013 ± 0.004 (ferrioxalate

actinometry). Luminescence of 1d was not observed in benzene at room temperature or in an EPA glass at 77°K.

The reactivity of S_1 and the unreactivity of T_1 for 1d complete an excited state structure - reactivity pattern already in evidence for $\text{1a}^{\text{1a,b}}$ and 1b^{1e} . The data further allow the relative location of states for 1d on the basis of the following (1) the effectiveness of laser emission (61 kcal/Einstein) at a wavelength which must be near the 0-0 transition (2) the quenching of valero-phenone photoelimination at near the diffusion controlled rate,⁶ (requiring $E_T(\text{1d}) < 70$ kcal/mol); and (3) the quenching of biacetyl ($E_T = 55 - 56$ kcal/mol) phosphorescence at a rate short of the diffusion limit.⁶ The following Jablonski diagram is consistent with the data for 1d and respects a reasonable n, π^* S - T separation.



Importantly, a very low lying triplet ($E_T < 50$ kcal/mol), either of a planar, "resonance" stabilized 8e variety, as suggested for 4N cyclic hydrocarbon pi systems,³ or similar to 1a ($E_T = 47$ kcal/mol^{1b}) does not obtain for 1d . However, a π, π^* triplet at 60 kcal/mol or less seems likely if 1d be diene-like.⁷ This raises the possibility of an intrinsically rapid⁸ intersystem crossing to an unreactive triplet manifold which would account in part for the low isomerization quantum yield and the lack of quenching by a heavy atom solvent (n-PrBr). Triplet counting experiments did not confirm the efficient formation of a reasonably

long lived triplet. Thus, Id was no more than 1/10 as efficient in sensitizing the dimerization of 1,3-cyclohexadiene ($E_T = 51 - 52 \text{ kcal/mol}$ ⁷) compared with benzophenone under parallel irradiation conditions. Intersystem crossing remains a possibility however, if the resulting triplet be very short lived or if energy transfer be insufficiently exothermic.⁶

The assignment and location of states for Id provide important reference points for the heterocyclic trienes generally. In addition, the indirect photochemical and photophysical methods employed here may be extendable to such systems with somewhat unusual chromophores where detection of luminescence may be impossible.

ACKNOWLEDGEMENT

This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by ONR.

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